Title: **Low Temperature Crystallographic Instability in ^{242}Pu$_{0.98}$Ga$_{0.02}$**

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Low Temperature Crystallographic Instability in ^{242}Pu$_{0.98}$Ga$_{0.02}$

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We have made an unsuccessful attempt to make a detailed characterization by neutron powder diffraction of the δ-α′ transformation that is known to occur at low temperatures in dilute Pu-Ga alloys. The α′-structure is a variant of the monoclinic a α′-phase, except that the lattice constants are a bit different, with some (or all) of the Pu sites partially occupied by Ga. This transformation is easily detected by dilatometric methods because of the 19% volume difference between the δ and α′-phases. In our study, we used ^{242}Pu in a Pu$_{0.98}$Ga$_{0.02}$ alloy to minimize neutron absorption and cooled the sample very slowly to maximize the degree of transformation. We did not detect any transformation to the α′-phase, but instead observed a slight line broadening effect that was visible in the raw data. The onset temperature of the line broadening (150K) coincides with observations of the δ-α′ transformation. We have developed two alternative explanations for the line broadening effect: (1) the occurrence at low temperatures of a cubic-tetragonal transformation in Ga-stabilized alloy or (2) the occurrence at low-temperature of a spontaneous anisotropic microstrain that is supported by the highly anisotropic elastic constants of δ-Pu.

KEYWORDS: plutonium, plutonium alloy, neutron diffraction, phase transformation

I. Introduction

It has been known for a long time that marginally stabilized Pu-Ga alloys transform at low temperatures from the FCC δ-phase to a monoclinic structure called the α′-phase.[1] This phase is very closely related to the α-phase that is always observed at room temperature and below for unalloyed element, but differs because some Ga is retained at the monoclinic atom sites.

The transformation appears to be martnezitic,[2] as allowed by the symmetry relations between the phases. This is somewhat surprising in view of the large difference in atomic volume between the phases: about 25% smaller for α′! In view of the large volume change, it is important to understand in detail the conditions that permit the occurrence of this transformation and their relationship to the aging of Pu.

The experiments described in this paper were undertaken to determine the crystal structure of the α′-phase by high-resolution neutron diffraction measurements. It turned out that the δ-α′ transformation was not observed in our experiments, but rather a subtle line-broadening effect was observed instead. The line-broadening effect is the subject of this paper.

II. Experimental Procedure
1. Sample

The Pu$_{0.98}$Ga$_{0.02}$ sample was prepared from electrorefined metal that was 99.85 wt.% plutonium with 95% ^{242}Pu, required to minimize absorption of neutrons; all other impurity levels were less than 100 ppm. Alloys were prepared by arc melting. Rods were cast either in a casting furnace or in the hearth of the arc furnace and machined to the final dimensions. The Pu alloy was heat-treated at 450°C for 200 hours, and then doubly encapsulated in thin-walled vanadium tubes for radiological protection.

2. Neutron diffraction

We made neutron powder diffraction measurements over a wide range of temperatures using the pulsed neutron diffraction technique at the Los Alamos Neutron Science Center (LANSCE) at Los Alamos National Laboratory. The NPD powder diffractometer has a path length of approximately 32m, and a resolution in d-spacing of about 0.15%. Measurements were made over the range 15-773K, using a closed cycle helium refrigerator to obtain low temperatures and a specially constructed furnace for high temperatures.[3]

The thermal history of the sample is important. The data presented in this paper were obtained from three separate experiments. In the first experiment, the freshly prepared sample was cooled very slowly to low temperatures, warmed to 150K, cooled again to 15K, and finally warmed again to room temperature. The cooling rate for the first cooling was 1 K/min. and about 2K/min. in the second experiment. In the third experiment, the sample was heated to 800K and furnace cooled slowly to room temperature.

3. Data analysis

Data were analyzed using the Rietveld analysis package in GSAS.[4] The Pu data are the same as those discussed in previous publications.[5,6] For each temperature, the refined parameters include lattice constants, scale factors, background, diffuse background, and Debye-Waller factor, and peak profile parameters. The absorption factor was fixed at $\mu R = 0.3$; this high value reflects the resonant absorption by isotopic impurities, primarily ^{239}Pu, in our ^{242}Pu sample.

The results of three types of refinement are presented in this paper. In the first series of refinements, the symmetry of the sample was cubic (Fm3m) and the profile function was isotropic in crystal space. In the second series, the symmetry remained cubic but the profile function of Stephens was used to fit the observed peak shapes, which were found to be anisotropic in crystal space. In a third series of refinements, a tetragonal distortion was allowed (I4/mmm) whenever significant line broadening was observed, but the peak-shapes were isotropic in crystal space.

III. Results

1. Observed diffraction patterns

We did not observe the expected α′-phase diffraction pattern on the first cooling to low temperatures, but only the diffraction pattern of δ-phase alloy. The diffraction patterns that we observed are shown in **Fig. 1**.

Because the diffraction pattern of the monoclinic alpha phase has many weak diffraction peaks, we make a special Rietveld analysis of the low temperature data that included 10 at. % of the α′-phase. We estimated the lattice constants of α′ at low temperature by including corrections for the anisotropic expansion observed as α → α′ at room temperature under pressure and the anisotropic thermal contraction observed as α is cooled to low temperatures. The estimated lattice constants for a'-Pu at 15K are a=6.142, b=4.797 and c=10.915Å with β=101.85º. In order to enhance the visibility of weak diffraction peaks, the data were compressed by a factor of 8 along the d-spacing axis.
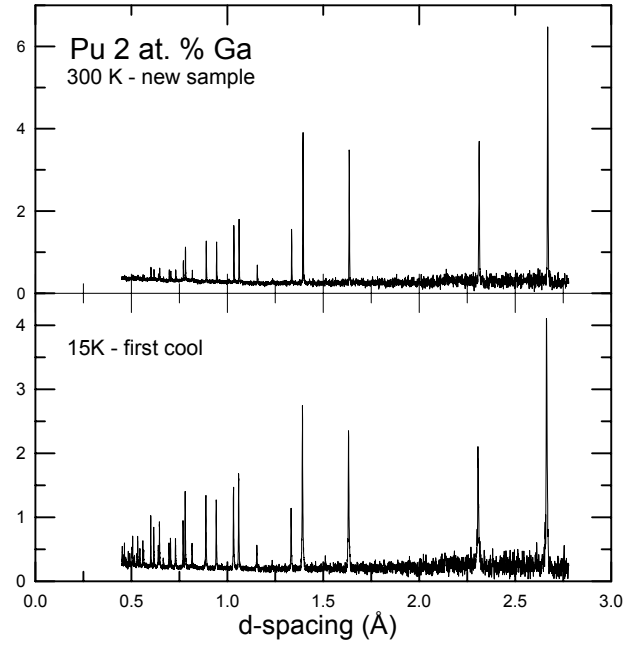

Fig. 1. Neutron diffraction patterns from NPD of Pu 2 at. % Ga at 300K (new sample) and 15K (first cool). The observed strong reflections are from δ-phase Pu. There are a few weak reflections for the vanadium containment
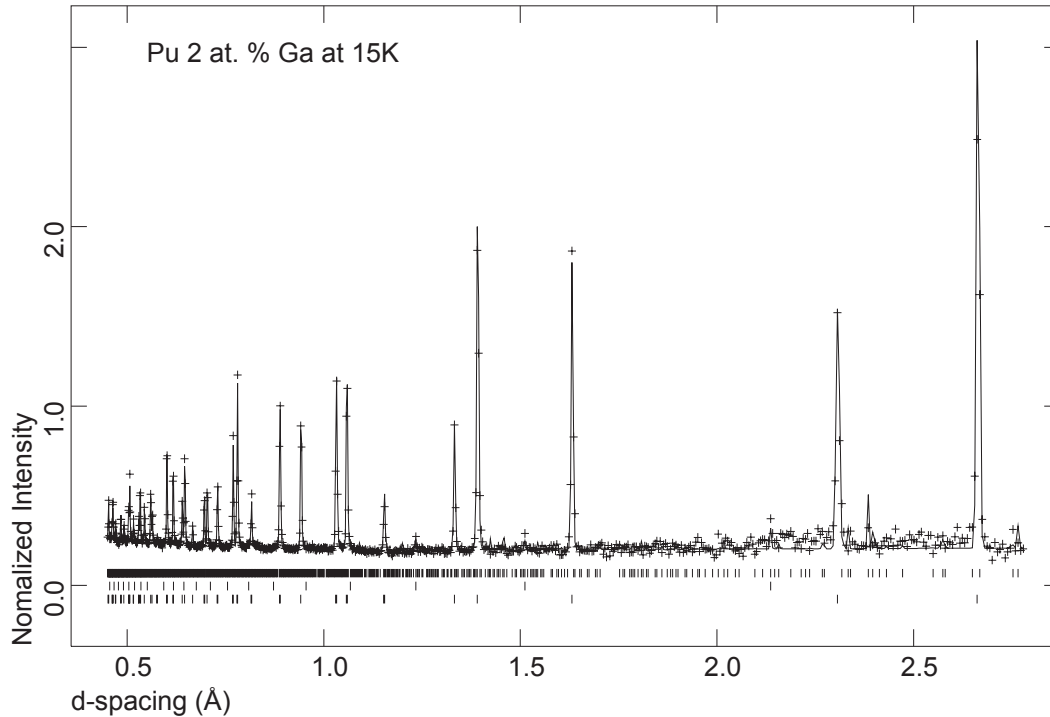

Fig. 2. Refined neutron diffraction pattern from Pu 2 at. % Ga at 15K. The three sets of reflection markers correspond to δ-phase Pu, vanadium, and α′-phase Pu.
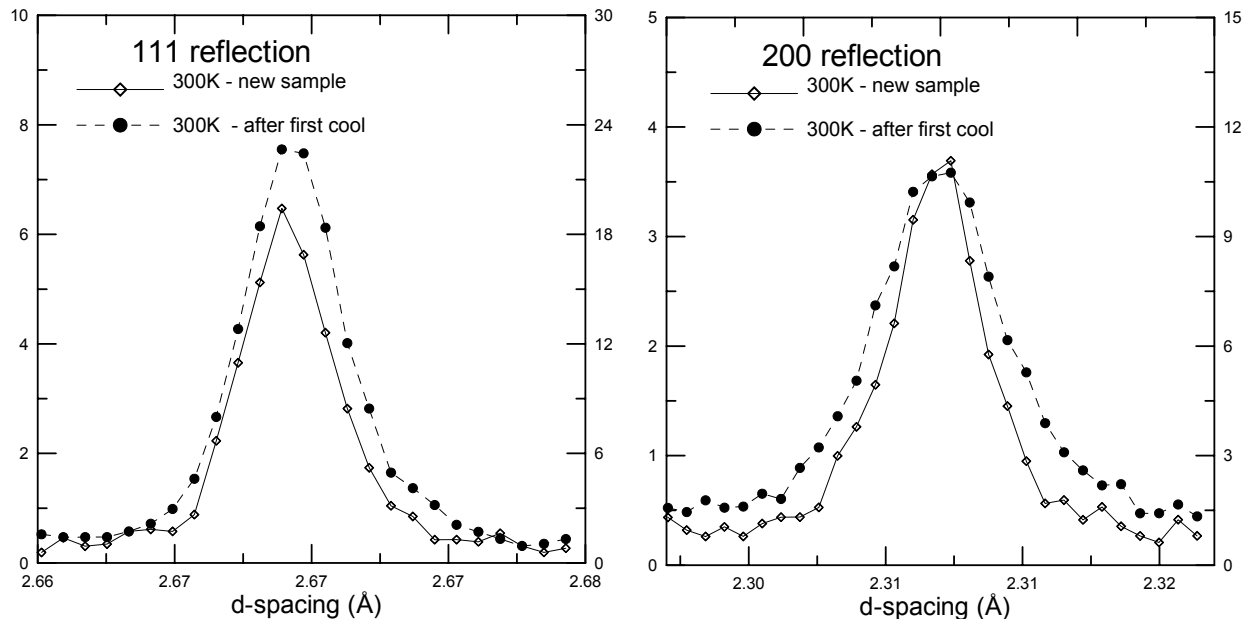
Fig. 3. 111 and 200 reflections for Pu 2 at. % Ga at 300K: new sample and sample warmed to 300K after first cooling.

This refinement is shown in Fig. 2. Three sets of reflection markers are shown: δ-phase Pu, vanadium (radiological containment), and the hypothetical α′-phase. As expected, the most of the calculated α′ peaks do not show up in the calculated pattern, but a few exceptions are found in the vicinity of d=1.6 and 2.4Å Since even these peaks are not observed, we can say that the phase fraction of α′-phase is less than 10 at. %. In fact, the refined value for the phase fraction of α′ is 0.2±0.4 at. % – essentially zero. However, it must be admitted that there is some uncertainty associated with the extrapolation of the α′ lattice constants to low temperature and that our estimate of the phase fraction will

Fig. 4. Microstrain versus temperature for the cubic isotropic model. (Figure redrawn from Ref. 6).)

be invalid if very small particles of α′ are involved.

There is observable peak broadening in the δ-phase at low temperatures that remains when the sample is warmed again. This is shown in **Fig. 3**, for the 111 and 200 reflections. Since the degree of peak broadening differs between the two reflections, we can say that the peak broadening is anisotropic in crystal space.

2. Results of Rietveld refinement.

First we mention that the refined lattice constant of the nominally 2 at. % alloy studied here is 4.625 Å. This means that the alloy composition, determined independently from its lattice constant,[7] is 1.8 at. % Ga.

(1) Cubic structure - isotropic microstrain

The average microstrain was determined as a function of temperature using a Rietveld model for which the crystal symmetry is held cubic and the peak width is assumed to be isotropic in crystal space. The term "microstrain' signifies the normalized variance of the lattice constant, under the assumption that the diffraction patterns is formed from an ensemble of grains with a Gaussian distribution of lattice constants. **Figure 4** shows the microstrain is plotted versus temperature.

The initial value of the microstrain was 500×10^{-6}, or simply 500 in the usual "micro" units, at 300K. This represents the initial state of the sample. During the first slow cooling, the microstrain increased very little until the temperature of 150K was reached, and then it increased very rapidly to a value of 2500 as the sample was cooled to 15K. The sample was then warmed to 175K, but the microstrain recovered only partially to a value of 2000, and reverted to 2500 when cooled again to 15K. When the sample was
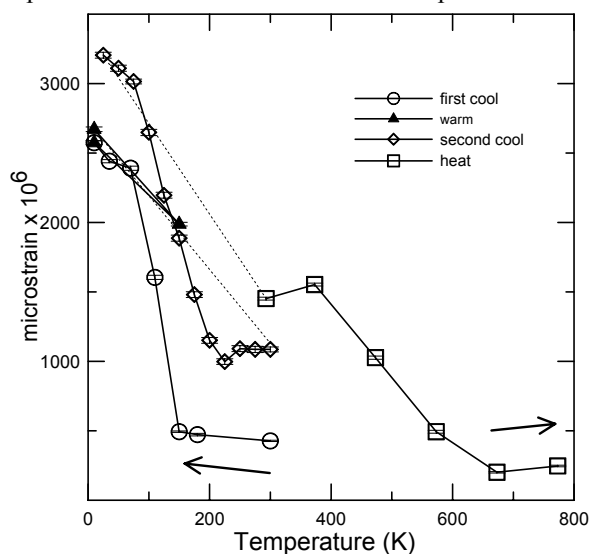
warmed to 300K, the recovery was again incomplete, as the value 1000 was reached. On the second complete cooling, the value of 3000 was reached for the microstrain at 15K. On the second warming to room temperature, the microstrain recovered only to 1500. Finally, on heating to over 600K, we observed that the microstrain recovered completely to a value less than 500.

(2) Cubic structure - anisotropic microstrain

We did a series of refinements using the anisotropic peak shape function of Stephens.[8] The assumption here is that the individual grains can respond to the stresses imposed by their surroundings according with an elastic response that is governed by the anisotropic elastic constants of the material. Even for cubic materials, the elastic response can be anisotropic; this is particularly true for δ-phase Pu, which is the most elastically anisotropic of all the FCC metals[9]. The anisotropic microstrain is plotted in **Fig. 5**, which shows the microstrain plotted as a function of direction in crystal space. This plot shows that the variance of the lattice constants is greatest in the [100] directions and smallest in the [111] directions. This behavior is in qualitative agreement with that of the anisotropic elastic compliances measurement for δ-phase Pu.[9]

3) Tetragonal structure – isotropic microstrain.

No peak splitting indicative of a tetragonal distortion was observed at low temperatures, but the strong anisotropy observed for the line shapes suggested that refinements could be carried out with a tetragonal structure whenever significant line broadening was found. The results of this analysis are shown in **Fig. 6**. The structure assumed for this analysis has space group I4/mmm with a single atom type at position (0,0,0). The maximum tetragonality is found at 15K: c/a = 0.9976·√2. Since no line splitting was actually observed, the result of this analysis may just be an image of the anisotropic microstrain found in the previous section. In other words, Fig. 6 does not provide conclusive evidence for a tetragonal phase of Pu-Ga alloy at low temperatures.
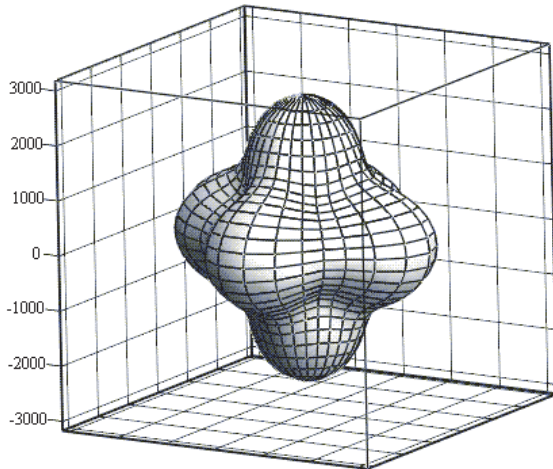

Fig. 5. Microstrain versus crystal direction at 15K for the cubic anisotropic model.

IV. Discussion

At the beginning of this experiment, we expected to see about 25% of the δ-phase transform to α´ at a temperature of about 150K. This did not happen, and the upper limit of α´ can be set at < 1%, subject to the limitations explained in section III.1. Instead, we saw a subtle line broadening effect that began to set in at 150K – the same temperature expected for the α´ transformation. We are unable, from the available data, to decide whether the observed line broadening signifies a cubic-tetragonal transformation (Fig. 6) or simply a spontaneous increase of microstrain (Fig. 5) in the cubic phase.

For the first explanation, the co-incidence of transformation temperatures suggests that the cubic-tetragonal transformation is a precursor to the δ-α´ transformation. We may then speculate that this transformation *always* occurs in δ-phase alloys at low temperatures, whether or not the δ-α´ transformation does. The occurrence of this "small" transformation would be a reasonable interpretation for the ultrasonic anomalies found by Rosen et al. in various δ-phase alloys.[11] It should be noted that the symmetries of the product phases of these two transformations are entirely different.

The second explanation requires the development of considerable internal stresses. Stokes and Wilson showed how to relate observed anisotropic microstrain, e(h,k,l), to hypothetical internal stresses, p_{11} and p_{12}, corresponding to dilatation and shear, respectively, supposed to represent grain interaction stresses. These are related by where the s_{ij} are the anisotropic elastic constants of the crystallites. (This, taken from Ref. 10, has been modified by

$$e^2(h,k,l) = (s_{11} + 2s_{12})^2 p_{11}^{\ 2} - 4s_{12}(s_{12} + 2s_{11})p_{12}^{\ 2}$$
$$- 4[(s_{11} - s_{12})^2 - s_{44}^{\ 2}]\frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2}p_{12}^{\ 2} \tag{1}$$
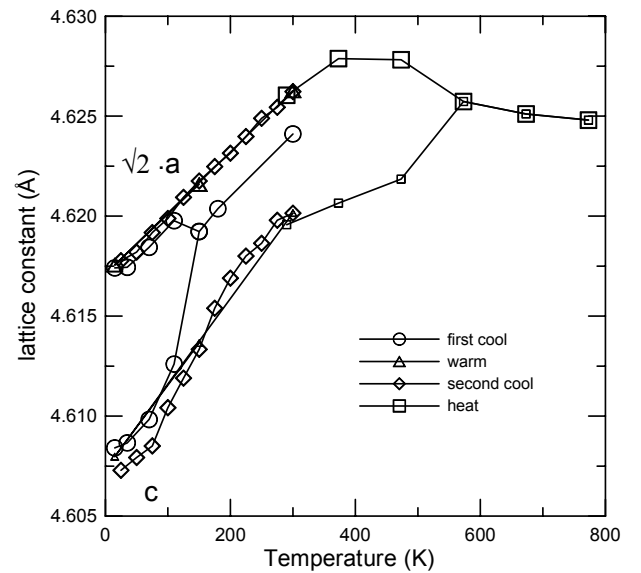

Fig. 6. Refined lattice constants of Pu 2 at. % Ga versus temperature for the tetragonal model.

the use of Voigt notation.) The stresses can be estimated from the observed anisotropic microstrain to be $p_{11}=65$ and $p_{12}=17.5$ MPa: values near the elastic limit for δ-phase Pu.

Another possibility for the analysis of the microstrain would be to use the formalism of Ungár and his collaborators based on dislocations.[12]

V. Conclusion

This study began as an unsuccessful attempt to make a high precision determination of the crystal structure of α´-Pu-2 at. % Ga alloy. The attempt failed because we observed a subtle line broadening effect, instead of the expected gross cubic-monoclinic transformation, at the expected transformation temperature. The exact nature of the low temperature phase is not yet clear, but two lines of further investigation will be pursued. We intend in the near future to look for this "small" transformation in a Pu-4 at. % Ga alloy where the δ-α´ transformation is not expected to occur. We also plan to check that the δ-α´ transformation actually occurs in [242]Pu by obtaining dilatometric data on identically prepared samples of [239]Pu- and [242]Pu –2 at. % Ga; since there is the possibility that the degree of radiation damage present in the sample determines the ultimate phase stability at low temperatures.[13]

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